CEMENT
AND
CEMENT MANUFACTURE

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Association of German Portland Cement Manufacturers.

AT the general meeting of the Association of German Portland Cement Manufacturers held in Berlin on March 15 and 16, 1932, a number of addresses were given, of which the following are abstracts:

REACTION BETWEEN LIME AND SILICA, ALUMINA, AND IRON OXIDE.

By Dr. G. Haegermann.

The reactions which occur during the clinkering of raw meal, between lime on the one hand and silica, alumina, and iron oxide on the other, are not yet completely understood. For this reason the compounds which are supposed to exist in cement were prepared in the pure state and their properties investigated. The following were especially studied: (1) Tricalcium silicate with hydraulic modulus 2.8 (for comparison the hydraulic modulus of cement is around 2.2). (2) Dicalcium silicate, which occurs chiefly in cements of insufficient lime content. (3) Tricalcium aluminate, hydraulic modulus 1.65. (4) Tetracalcium aluminate ferrite.

(1) Tricalcium silicate decomposes at 1,900 deg. C., splitting off lime which then causes expansion. Tricalcium silicate was prepared by heating the powdered raw mixture for three hours at 1,550 deg. C. Dyckerhoff's work has proved that the compound is only formed from the pure constituents at temperatures above 1,450 deg., although in the presence of alumina and iron oxide it is formed at the normal temperatures of cement burning. Between 1,000 and 1,500 deg. the stability of tricalcium silicate is only slight, since it tends to break up into CaO and $\beta 2CaO.SiO_2$. This confirms the theory of Michaelis which assigns the formation of free lime on the ignition of clinker to the decomposition of tricalcium silicate.

Samples of tricalcium silicate were gauged and submitted to the boiling test, which proved it to be entirely sound. Setting commenced after six hours, and was generally complete after ten hours. The compound is thus decidedly slow-setting, although its setting time can be modified by additions. Thus alkali sulphates and the chlorides of calcium, potassium, magnesium, and aluminium accelerate the set, while borax and potassium bichromate retard it.

(2) Tricalcium aluminate decomposes on melting to a eutectic of the composition $3CaO.Al_2O_3 + 5CaO.3Al_2O_3 + CaO$ (free). The temperature of fusion is

1,535 deg. C., in agreement with Rankin. The compound can be prepared without special difficulty by heating for a period at 1,350 deg. This constituent of cement is also completely sound.

On hydration there is an extremely rapid increase of temperature to 85 deg., and it is found that the test-pieces first harden, then after a time once more become soft and spongy, and finally very slowly harden again. Storage under water gives considerably lower strengths than combined storage (1 day moist air, 6 days water, 21 days air). Gypsum and calcium chloride retard hydration, and an addition of 5 per cent. gypsum gives rise to severe expansion. If hydrated tricalcium aluminate is powdered and again gauged with water, gradual hardening occurs. The eutectic mentioned previously is quick setting, and it is found that no dicalcium aluminate exists.

Jänecke's compound, $8CaO.2SiO_2.Al_2O_3$, is not formed at 1,600 deg., but a product containing free lime is obtained instead, while on slowly cooling the free lime is reabsorbed, and $5CaO.3Al_2O_3$ is transformed to $3CaO.Al_2O_3$. The break in the cooling curve can in no wise be accepted as a criterion for the existence of Jänecke's compound. On heating a mixture of the theoretical composition of Jäneckeite the following compounds are formed at 1,600 deg.: $2(3CaO.SiO_2)$, $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, and free lime.

Admittedly American experiments of this kind gave a somewhat different result, but the difference can be explained by the fact that entirely different conditions exist when the mix is held at the temperature of experiment for a prolonged period; the free lime is absorbed by the aluminates, and di- and tricalcium silicates and tricalcium aluminate are formed. The quantity of dicalcium silicate is increased by maintaining the mix at 1,175 deg. However, both series of experiments establish that Jänecke's compound has no existence, and thus cannot be a cause of hardening.

(3) As regards the iron oxide-containing constituents of cement, it must first be emphasised that dicalcium ferrite plays no part among them. In spite of the many divergent opinions which have been expressed it may now be accepted as proved that celite has the composition $4CaO.Al_2O_3.Fe_2O_3$. On "annealing," this compound is capable of absorbing 3 to 4 per cent. more CaO than is represented by the formula; this is, however, possibly combined as tricalcium aluminate. A further proof of the existence of the tetra-compound is afforded by the fact that at 1,320 deg. C. free lime separates from a mixture of $2CaO.Fe_2O_3$ and $3CaO.Al_2O_3$.

To summarise, tricalcium silicate is the real source of hardening, while the aluminates play an essential part in promoting this hardening.

THERMAL BASIS OF CEMENT BURNING.

By Professor W. Eitel (Director of the Kaiser Wilhelm Institute for the Chemistry of the Silicates).

Professor Eitel criticised the usual method of calculating the heat balances of rotary kilns, and showed that this may not be accurate, since new determinations of the constants involved have given much higher results than those hitherto accepted. Only the values given by W. P. White satisfactorily agree with those recently obtained.

The problem is complicated by the question of the specific heat of the raw meal, for up to the present the only figures available relate to the separate constituents. The clay presents special difficulty on account of the endothermic reaction of dehydration of the metakaolin which occurs at 510 deg. C. This

endothermic effect has hitherto been ignored, but is actually much higher than has been supposed. This is also the case with the exothermic change which occurs in the metakaolin at 950 deg., and which is considered to be due to the decomposition of kaolinite into its oxides. It should be noted that this decomposition, with the accompanying exothermic effect, begins to take place at temperatures below 950 deg.

In cement raw meal the exothermic decomposition of metakaolin takes place simultaneously, at 950 deg., with the exothermic reactions of calcium silicate and aluminate formation. The fundamental work of Nacken deals only with the sum of all the heat reactions and leaves the matter of the fractions of this sum due to the individual constituents still to be determined.

In conclusion, Professor Eitel gives a new method of representing the process of cement burning both as in theory and in practice. He finds the difference between theory and practice may be eliminated by calculating practical results from 20 deg. C. instead of from 0 deg., and by allowing for the moisture in the raw meal and the magnesium carbonate in the limestone.

HYDRAULIC HARDENING AS A SURFACE REACTION.

By Professor H. Kühl.

Professor Kühl spoke in support of the 25-year-old theory of Michaelis which regards the hardening of cement as a problem in colloidal chemistry. He gives the following argument, among others, for a colloidal shrinking process. A high-limed vitreous melt is finely ground and gauged with silica-free caustic potash solution. X-ray examination shows no trace of crystal formation after four weeks, although even at three days the tensile strength was 272 lb. per sq. in. The hardening of calcium aluminates is also a colloidal phenomenon, the best example of which is afforded by aluminous cements. The entire phenomena of shrinking and swelling can only be explained on the hypothesis of colloidal hardening, since they are undoubtedly due to surface reactions such as can only proceed when the particle size is less than 0.1 μ. Care must be taken not to imply the conception " amorphous " in discussing such colloids, as they may possess a fine crystalline structure.

The first products formed during the hardening of cements are, however, obviously amorphous. Siliceous cements, such as are capable of colloidal swelling, are always, apart from Portland cement, low-limed silicates. In the case of Portland cement a system capable of colloidal swelling is produced as a result of a primary process in which part of the lime passes into solution.

Professor Kühl and his co-workers treated coarsely-ground cement grit with the reaction liquids formed when cement is gauged in the usual way. By careful decanting and filtering they separated three phases, *viz.*, the reaction liquid, the product of hydration, and the coarse cement grit.

The following reaction liquids were employed: (*a*) With Portland cement—saturated lime-water. (*b*) With aluminous cement—pure water. (*c*) With blast-furnace slag—the solution obtained by treating ground slag with distilled water; among other compounds, this contains calcium sulphide in solution. Lime-water was allowed to diffuse into the solution to accelerate the reaction.

(*a*) In the case of Portland cement the hydration products separated after eight hours and contained twice as much alumina as silica, although the original cement contained three times as much silica as alumina. After twenty days the proportions existing in the original cement had been established in the product of hydration. The increase in the lime content of the reaction liquid which takes

place on gauging the cement can only be explained by decomposition of the tricalcium silicate, thus confirming the views of Michaelis. The aluminates pass first of all into solution, from which hydroaluminates then separate. The hydration of tricalcium aluminate is very vigorous, although not nearly so violent as that of tricalcium silicate. By contrast, Brownmiller's compound, with its ferrite constituent, is only very slowly hydrated. The lime dissolved from the tricalcium silicate is at first replaced in the molecule by water. Finally, however, the molecule is decomposed with the formation of hydrosilicates, which surround the individual grains of cement with a layer of gel.

(*b*) With aluminous cement, monocalcium aluminate vigorously dissolves with the formation of dicalcium hydroaluminate and aluminium hydroxide. At a later stage gel separates from this solution, and it is upon this gel that the ageing of the cement depends in that a gradual transformation into crystalline compounds takes place. The products of the hydration of aluminous cement contain only very small amounts of silica.

(*c*) In the case of blast-furnace slags of high lime content the alumina tends to form high-limed hydroaluminates, while with slag low in lime hydrosilicates of low lime content are formed. The products of hydration depend on the concentration of lime in the liquid phase, and may be either those obtained from Portland or from aluminous cement. In both cases they are colloidal in character.

In the hydration of all cements the aluminates pass into solution, are then hydrated, and then separate as new colloidal compounds. The silicates, by contrast, absorb water into the system and are then hydrated, with the splitting off or absorption of lime, to form a colloidal gel-mass which encases the reacting grain of cement.

WAYS IN WHICH WATER IS COMBINED IN CEMENT.

By Professor Nacken.

Although the problem of the constitution of cement may be considered to be solved, there is still considerable uncertainty regarding the phenomena of setting and hardening. It is therefore necessary to investigate this question along the following lines:

(1) Studying the reaction between finely-ground cement and water.

(2) Establishing the nature of the new compounds formed.

(3) Investigating the chemical and physical properties of these new compounds.

The majority of workers on the subject have investigated the vapour tension of the system in its relation to temperature and volume.

The compounds containing water may be classified as hydroxides, hydrates, zeoliths, water-containing glasses, and gels; and the water is held with varying degrees of stability in the several classes. These groups are further distinguished by differences in degree as regards their capacity for swelling, exchange of bases, and staining, as well as in their behaviour on ageing. For example, zeoliths and gels differ in their capacity for swelling, arising from the fact that zeoliths are saturated on separation from aqueous solution and are not subject to renewed swelling, while the capacity of gels for swelling decreases with age unless this property is renewed by means of chemical dispersion agents. While gels gradually give up their water, this does not occur with hydrates and zeoliths. In Portland cement, with its complex constitution, the entire range of these possibilities as regards combination of water may occur.

The methods of investigation may depend either on analytical decomposition or on synthesis. Among the former vapour pressure measurements play an important part. The curves obtained in this method may be either isobaric heating curves (*i.e.*, under constant pressure), or isothermal (*i.e.*, under constant temperature with changing pressure). Isobaric curves show a break when a new hydration product either appears or disappears; in obtaining these curves the attainment of equilibrium must naturally be awaited. The decomposition may also be followed by subjecting the substance to a high vacuum and determining the loss of water after progressive intervals of time.

In making deductions from vapour-pressure curves the requirements of the phase rule must naturally be fulfilled. This is the case for hydrates and hydroxides, but not for gels. Zeoliths are generally in a state of stable equilibrium and only undergo a change in water content when heated or subjected to vacuum. With gels well-defined characteristic curves are not obtained, so that any breaks in the curves must be considered in the light of the particular example under consideration.

In the synthetic method the phenomena that occur on mixing cement with water are observed, characteristic of which is the evolution of heat. With cement free from gypsum there first occurs a considerable evolution of heat, which then decreases for a time and finally slowly increases again. This may be accepted as showing that a layer of silica-sol is first formed around the clinker particles, and that further water then diffuses through this layer. The diminution of the evolution of heat undoubtedly indicates a strengthening of the gel layer around the particles due to the flocculation of the silica-sol by the strong electrolytes. If sodium carbonate is added at this stage an entirely different result is obtained, since the silica is thereby converted into a soluble salt, and the slowing up due to the gel film is avoided.

Investigations into swelling show that gel is the main constituent of the cementitious substance, although it is possible that zeoliths are also involved. This uncertainty could only be definitely cleared up if it were possible to determine the density of the zeoliths. Such experiments cannot fail to be useless, however, since they must be carried out in some liquid which is absorbed by the zeoliths.

A new method of following the setting of a cement consists of determining the dielectric constant, which for pure water has the value 80. Hydrates reduce this value in proportion as their quantity increases. Gels rich in water, on the other hand, raise the dielectric constant, although it falls again when the water is very firmly held, as, for example, in opal. In the case of cement the curve first of all increases above 80, followed by a gradual fall, which may, however, occasionally proceed rapidly. Even although the slightest variations in the experimental conditions give greatly varying results, the basic tendency described is always unmistakable.

Proposed New Australian Cement Works.

A plan involving the expenditure of approximately £300,000 in the erection of cement works in the Maryborough district was recently outlined by Mr. C. D. W. Ranklin, managing director of the Queensland Collieries Co., at a Rotary Club luncheon at Maryborough. Mr. Ranklin said the British Board of Trade had agreed to advance £120,000 on condition that Messrs. Newell & Co., Ltd., Doncaster, agreed to complete the plant and deliver it at Urangan jetty for £200,000.

The Rotary Kiln in Cement Manufacture.—XII.

By W. GILBERT, Wh.Sc., M.Inst.C.E.

Recording Instruments.—(167) In the last article a dry-process kiln plant (A) was referred to, and three recorder charts were given to illustrate the working of the kiln. The kiln speed as seen from Fig. 53 was very irregular, and an enquiry is now being made into the cause of it. The kiln details below will be useful for reference:

(*a*)	Length over all	97 ft. 6 in.
(*b*)	Diameter inside lining, raw meal end	6.16 ft.
(*c*)	Slope	1 in 25
(*d*)	Fast speed	1 r.p.m.
(*e*)	Slow speed	½ r.p.m.
(*f*)	Average speed during test	0.89 r.p.m.
(*g*)	Clinker output per hour	45 cwt.
(*h*)	Exit gas temperature (not corrected)	1141 deg. F.

(168) It is first desired to find out if the kiln could run continuously either at 1 r.p.m. or at ½ r.p.m. if the working conditions were uniform, and if there is any advantage in one speed over the other. A calculation is made of the percentage charges which would be retained in the kiln at the raw meal end when it is operated at (*d*) the fast speed, (*e*) the slow speed, and (*f*) the average speed. The clinker output was 45 cwt. per hour, corresponding to 67.8 cwt.

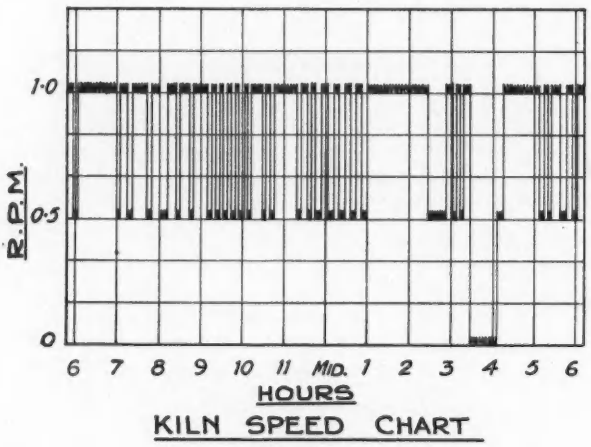


Fig. 53.

of raw meal. Taking the latter to weigh 85 lb. per cu. ft., the volume of the feed per minute is $\frac{67.8 \times 112}{60 \times 85} = 1.49$ cu. ft. The average speed of the kiln throughout the test was 0.89 r.p.m., so that the average feed per revolution (denoted by (*f*)) was $\frac{1.49}{0.89} = 1.68$ cu. ft. The corresponding charge in the kiln

at the raw meal end may be obtained from Fig. 50 (the graph may be used either for dimensions in centimetres or in feet). Using the latter, the kiln diameter is 6.16, so that $\frac{100 \times f}{d^3} = \frac{100 \times 1.68}{(6.16)^3} = 0.72$. From the graph the corresponding charge is 4 per cent.

(169) Making similar calculations for the fast and slow speeds the table below is obtained:

R.M.P. of kiln.	Charge per cent. at raw meal end.	Advance of charge per revolution feet.
(1)	(2)	(3)
1.00	3.56	1.44
0.89	4.00	do.
0.50	7.12	do.

The advance of the charge per revolution in column 3 is taken at 23.3 per cent. *d*, as stated in paragraph (159). These charges are those which would obtain over about 70 per cent. of the length of the kiln provided the speed were kept constant for a sufficient length of time. Near the delivery end the charge would be increased by the restricted outlet which was fitted, but it would be reduced by the loss of the CO_2, hence for the present purpose the charge as calculated may be assumed to apply throughout the kiln.

Influence of Charge Volume on Rate of Heat Transmission.

(170) At this stage the subject is briefly referred to in order that the speed chart of kiln A (see Fig. 53) may be properly considered. A cross-section of the kiln 30 ft. from the feed end is selected as representative. At this point the hot gas temperature is approximately 1,700 deg. F., and the material temperature 800 deg. F. Referring to Fig. 55, part of the heat is transmitted directly from the hot gases to the upper surface A B of the charge by radiation and convection, but a considerable proportion is first transferred to the kiln lining A D B above the charge, and from the lining (mainly by radiation) to the upper and under surfaces of the charge. If the charge in the kiln is increased the area of its upper surface A B and the quantity of heat received by it is increased, but the area of the kiln lining A D B above the charge (which is available for receiving and retransmitting heat) is reduced; hence a point is reached when a considerable increase in the volume of the charge adds little to the heat transmitted to it.

The rate of heat supply in B.T.U.s per foot run of kiln per minute at the cross-section considered has been calculated for various charges, and the result is shown in Fig. 56. The heat lost by shell radiation is added (at this cross-section the kiln lining is 4½ in. thick). The radiation loss is a large proportion of the total heat supply, because the percentage coal consumption of the kiln is low.

(171) From the percentage charges given in paragraph (169) for the raw meal end of the kiln and from the data given on Fig. 56, the particulars in the next table are obtained:

It will be seen that it would be slightly more economical to run the kiln continuously at 0.5 r.p.m., since, compared with the fast speed, an increase of output of 7 per cent. would be obtained for an increase of 4 per cent. in the coal feed. These figures are approximate only, and refer to one cross-section of the kiln, but they give a good general idea of the position.

(172) Referring again to Fig. 53, it will be now evident that the excessive variation in the kiln speed is not caused by unsuitable fast or slow speeds of the kiln, since a small alteration to the coal feed would allow the kiln to run con-

Speed of kiln R.P.M.	Charge per cent.	Heat supply to charge B.T.Us. per foot run of kiln per minute.	Relative heat supply.	Total heat supply including radiation loss.	Relative total heat supply.
1.00	3.56	720	100	950	100
0.50	7.12	768	107	988	104

tinuously at either speed if the demand for heat were uniform. The inequality is probably caused by a variation in the demand for heat at the clinkering zone, which may be due to the excessive variations in the composition of the raw

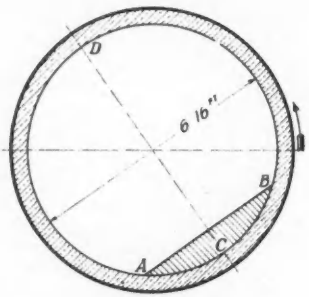


FIG: 55

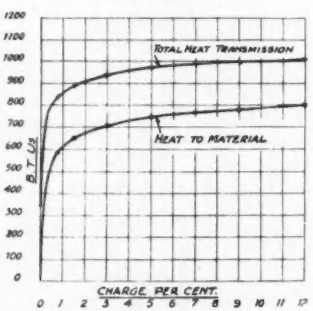


FIG: 56

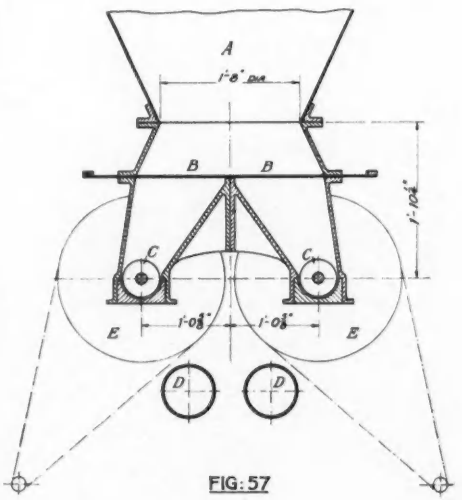


FIG: 57

material (see paragraph (163)) or to irregularities in the rate at which the latter comes down the kiln. When a demand for additional heat in the clinkering zone occurs it is best met by running the kiln at half speed, since the advance of the charge per minute is at once halved and the heat supplied per lb. of material per minute is doubled. Presuming the raw meal feed to be unaltered, the charge in the kiln at the feed end also tends to double, but this increased charge would not reach the clinkering zone (at the kiln average speed) for about 63 minutes.

Effect of Increasing Coal Feed.—(173) In the case of kiln plant A the coal feed is considered to be reasonably uniform, see paragraph (164). The normal air supply could not be increased beyond 7 per cent., hence the additional heat passed to the kiln by increasing the coal-screw speed would not exceed 7 per cent., and of this quantity only a proportion would be transferred to the material in the clinkering zone.

Result of Investigation.—(174) One conclusion to be drawn from this investigation is that at the normal running speed a rotary kiln should retain a uniform charge of about 7 per cent., provision being made for speed reduction as required in order to cope with relatively underburned material.

Kiln Plant B.

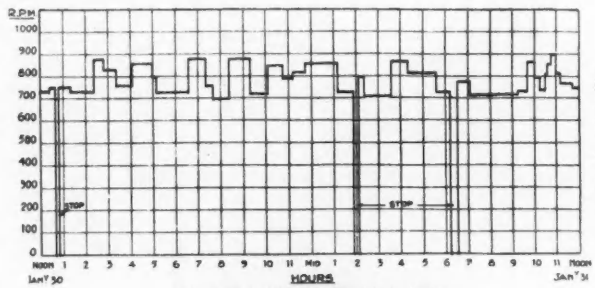
(175) The performance of a fairly modern wet-process kiln is next considered. The kiln dimensions and the chief test results are as follows:

(*a*)	Kiln, length over all	230 ft.
(*b*)	,, diameter inside shell	8 ft. 11 in.
(*c*)	,, clinkering zone, length	37 ft. 6 in.
(*d*)	,, ,, ,, diameter inside shell..	10 ft. 0 in.
(*e*)	,, slope	1 in 25.
(*f*)	,, fast speed	0.79 r.p.m.
(*g*)	,, slow speed	0.37 r.p.m.
(*h*)	,, slurry-lifters, total area	1,032 sq. ft.
(*i*)	Slurry moisture	44.0 per cent.
(*j*)	Excess air used	18.0 per cent.
(*k*)	Exit gas temperature, not corrected	755 deg. F.
(*l*)	Fine coal, residue on 180² sieve	13.0 per cent.
(*m*)	Clinker output per hour	175.7 cwt.
(*n*)	Unit output of kiln	14.3
(*o*)	Standard coal consumption	31.75 per cent.
(*p*)	,, ,, referred to a slurry moisture of 40 per cent.	29.12 per cent.

(176) The slurry-lifters were triangular steel-plate brackets, four in circle. The area is reckoned on the outer surfaces of the plates only, for as the insides of the triangles were partly choked with semi-dry slurry the gas circulation through the triangular area would be small. The kiln test of one week was made in winter during very wet weather, and this partly accounts for the excessive slurry moisture and consequently to some extent for the low unit output of the kiln.

Coal Feed Gear.—(177) A cross-section of the apparatus for feeding fine coal to the kiln is shown in Fig. 57. The hopper was relatively small, provided with a steeply inclined conical base, and an opening at the bottom 20 in. in diameter. Each feed-screw was provided with a shroud-pipe 7 ft. long from which delivery was made to the coal-firing pipe. This type of coal-feed has not proved satisfactory, probably because the screws are too far from the base of the hopper.

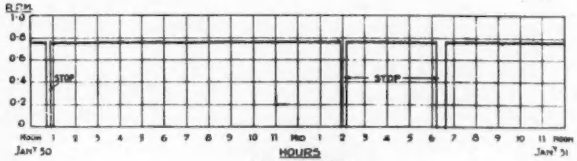
The apparatus was designed to operate with a full hopper, and an overflow arrangement was provided on the filling conveyor for this purpose. The kiln gave considerable trouble for some time after it was started, and eventually the works manager decided that an irregular coal feed was mainly responsible. The fine coal frequently clogged in the base of the hopper, and it was finally decided to grind the coal as required, the depth of the coal in the hopper being maintained at 3 to 4 ft. only. A certain amount of attention was necessary, but the result was apparently successful, and the coal feed was operated in the manner described when the test was made on the kiln.



HOURS

COAL FEED SCREWS, RELATIVE SPEED
KILN PLANT B

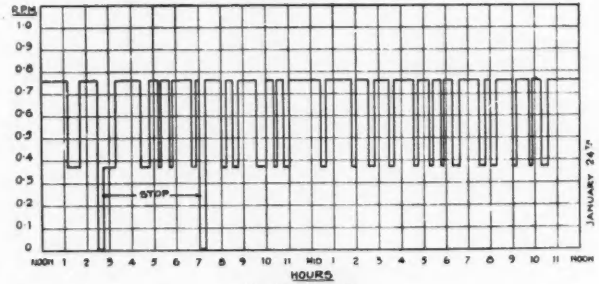
FIG: 58



HOURS

KILN SPEED
KILN PLANT B

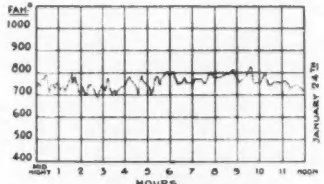
FIG: 59



HOURS

KILN SPEED
KILN PLANT C

FIG: 60



HOURS

KILN EXIT GAS TEMPERATURE.
KILN PLANT C

FIG: 61

(178) Speed recorders were driven from the shaft of each coal-feed screw and the revolutions per minute shown on each chart were proportional to the coal-screw speed. The revolutions taken from each chart have been added to give the combined diagram shown in Fig. 58, and (if the coal feed is accepted as uniform) the diagram shows at any instant the proportionate rate at which the fine coal was fed to the kiln.

Kiln Speed.—(179) The kiln was provided with two speeds, 0.37 and 0.79 r.p.m. A speed recorder was driven from a countershaft of the kiln-driving gear; Fig. 59 shows the chart obtained for one period of 24 hours. It will be seen that the kiln was on the fast speed for the whole of the running time, so that any variation in the demand for heat was met by altering the speed of the coal-feed screws. This method of working proved satisfactory, since, owing to the precautions taken, the delivery of fine coal was probably proportional to the speed of the screws. No direct test was, however, made on the uniformity of the coal feed at this kiln plant.

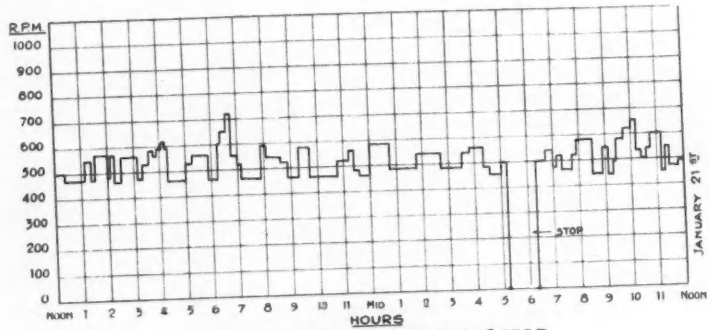
Kiln Plant C.

(180) In the case of kiln plant C (wet-process) investigation was made into the working of the fine-coal feeding apparatus. The kiln dimensions and chief test results are as follows:

(*a*)	Kiln, length overall	228 ft. 6 in.
(*b*)	,, diameter inside shell	8 ft. 11 in.
(*c*)	,, clinkering zone, length	32 ft. 2 in.
(*d*)	,, ,, ,, diameter inside shell..	10 ft. 0 in.
(*e*)	,, slope	1 in 25
(*f*)	,, fast speed	0.76 r.p.m.
(*g*)	,, slow speed	0.37 r.p.m.
(*h*)	,, slurry-lifters, total area	454 sq. ft.
(*i*)	Slurry moisture	39.2 per cent.
(*j*)	Excess air used	14.0 per cent.
(*k*)	Exit gas temperature, not corrected	755 deg. F.
(*l*)	Fine coal, residue on 180² sieve	8.6 per cent.
(*m*)	Clinker output per hour	148.0 cwt.
(*n*)	,, unit output	13.2
(*o*)	Standard coal consumption	29.4 per cent.
(*p*)	,, ,, referred to a slurry moisture of 40 per cent.	29.9 per cent.

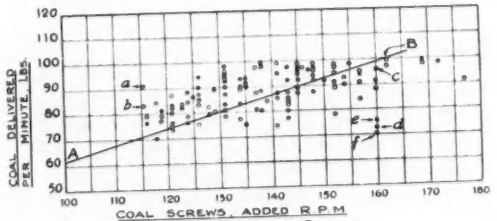
The kiln was fitted with a number of curved cast-iron slurry lifters of the bracket type; the area listed is reckoned on both sides of the plate. The low unit output was mainly due to irregular working of portions of the kiln apparatus, as will presently appear.

Slurry Feed.—(181) The slurry feed was of the orifice and constant head type, similar to that illustrated in Fig. 2 (see January, 1930, number). The discharge chute (G) could in kiln plant C be turned on a vertical hinge, or deflected by a wire rope operated from the burning platform in which event about one-third of the slurry leaving the feed tank passed to the overflow and two-thirds to the measuring vessel and then to the kiln. The discharge chute, or nozzle, was usually deflected when the kiln operated at half speed. The feed slide was set by the burner to supply slurry for a clinker output of about 9½ tons per hour, hence frequent deflections of the nozzle formed one of the disturbing influences in the working of the kiln. Measurements of the rate at which the slurry was being fed to the kiln were made hourly during the first five days of the test,



COAL FEED SCREWS, RELATIVE SPEED
KILN PLANT C

FIG: 62



COAL SCREWS, ADDED R.P.M
KILN PLANT C

FIG: 63

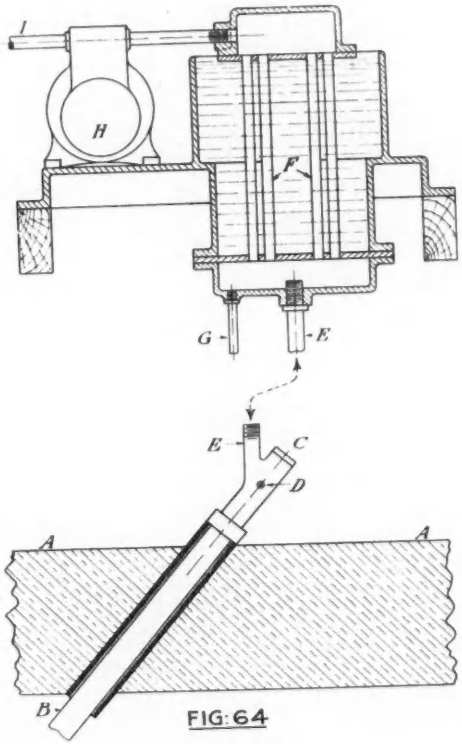


FIG: 64

the result being that with the normal opening of the feed slide the rate of feed (reduced to clinker) might vary from 9 to 10¼ tons per hour.

Coal Feed.—The coal-feeding apparatus was a duplicate of that used on Plant B (see Fig. 57); in this case, however, the kiln hopper of 5½ tons capacity was always kept full, or nearly so.

(To be continued.)

Notes from Abroad.

United States Cement Production and Sales.

The production of cement in the United States for the two months January and February, 1932, is given by the U.S.A. Bureau of Mines as 8,997,000 barrels, compared with 12,515,000 barrels for the same period in 1931. The sales amounted to 6,511,000 barrels in the same period for 1932, and 9,766,000 barrels in 1931.

Cement Sales in Germany.

The cement sales of the Deutscher Zement Bund for the three months January to March is reported to be 385,000 tons in 1932, 632,000 tons in 1931, and 1,188,000 tons in 1930.

The sales of the Norddeutscher Zement-Verband for January to March, 1932, amounted to 57 per cent. of the sales for the same period in 1931.

It is stated that sales of the Suddeutscher Zement Verband for the first quarter of 1932 were 60,000 tons, or half those for the same period in 1931. The sales for 1931 showed a decrease of 32.6 per cent. on those in 1930, *i.e.*, 890,000 tons compared with 1,320,000 tons.

The cement sales of Heidelberg-Mannheim-Stuttgart A.G. during 1931 amounted to approximately 400,000 tons, compared with 550,000 tons and 850,000 tons in 1930 and 1929 respectively.

Belgian Cement Output.

The output of cement in the month of March, 1932, was 33 per cent. of total capacity. This compares with 44.5 per cent. of total capacity in March, 1931. Deliveries for March, 1932, were 40 per cent. of capacity, compared with 38.8 per cent. of capacity in March, 1931.

Cement Sales in Poland.

The value of the home sales of Portland cement in Poland amounted to 314,000 Zloty (£7,238) for the period January 1 to February 23 this year, compared with 1,960,000 Zloty (£45,182) and 2,930,000 Zloty (£67,542) respectively for the same periods in 1931 and 1930.

Cement Production in Italy.

The production of Portland cement in Italy during the year 1931 was 3,076,715 tons, compared with 3,482,364 tons in 1930.

Cement Output in Greece.

The cement output of S.A. des Ciments de Chalkis Artificiels, Greece, during 1931, was 46,000 tons, which compares with 26,000 tons in 1930.

Cement Production and Sales in Spain.

The sales of cement in Spain is given as 1,431,113 tons in 1931, compared with 1,494,327 tons in 1930. Production is given as 1,400,674 tons in 1931 and 1,608,041 tons in 1930.

Determination of Setting Time of Portland Cement.

By A. C. DAVIS, A.M.I.Mech.E., M.Inst.C.E.I., F.C.S.

WORKS MANAGING DIRECTOR, ASSOCIATED PORTLAND CEMENT MANUFACTURERS, LTD.

THE activity shown in the transition from a paste to a hard mass when Portland cement is mixed with water indicates whether the material is of a quick or slow-setting nature, and it is important to be able to determine into which class a cement falls. The cement user must be aware of the setting characteristics of the cement he proposes to employ in constructional work, for unexpected results may ensue from lack of this information. If a quick-setting material is unwittingly used, the setting may commence before the mixing and deposition

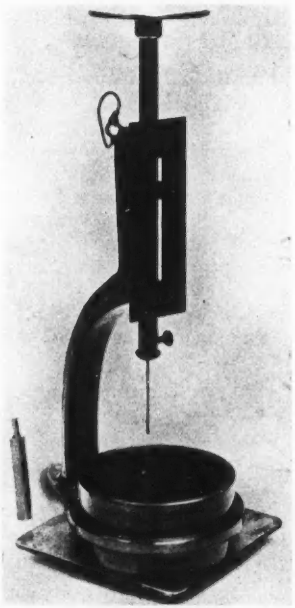


Fig. 1.

of the concrete are completed, and if this setting action is unnoticed it may be interfered with and the material will not again set for some time. The cohesive value of the cement may then be so greatly reduced as to render the work very weak. Care must be taken to ascertain the setting time of the cement before it is to be used, and also to ensure that no more mortar is mixed than can be used before it begins to set.

Cement which has been allowed partially to set is sometimes retempered or remixed for use, but this is not to be recommended unless the remixing can be done with further additions of water, otherwise the strength of the resultant material may thereby be considerably lowered.

Cement manufacturers usually endeavour to produce a slow-setting cement which takes at least thirty minutes to harden when gauged in a neat paste. Quick-setting cement which commences to harden in a few minutes is only made if specially ordered. Although perhaps capable of considerable tensile resistance, and therefore of value in constructional work, yet quick-setting cement must be used with care. It is employed only for special purposes, such as in operations liable to be quickly submerged by tidal water. In all cases slow-setting cement is preferable, if circumstances will allow its use, for it is obviously safer when used by workmen not under supervision, or by those who like to prepare their mortar well ahead of their requirements.

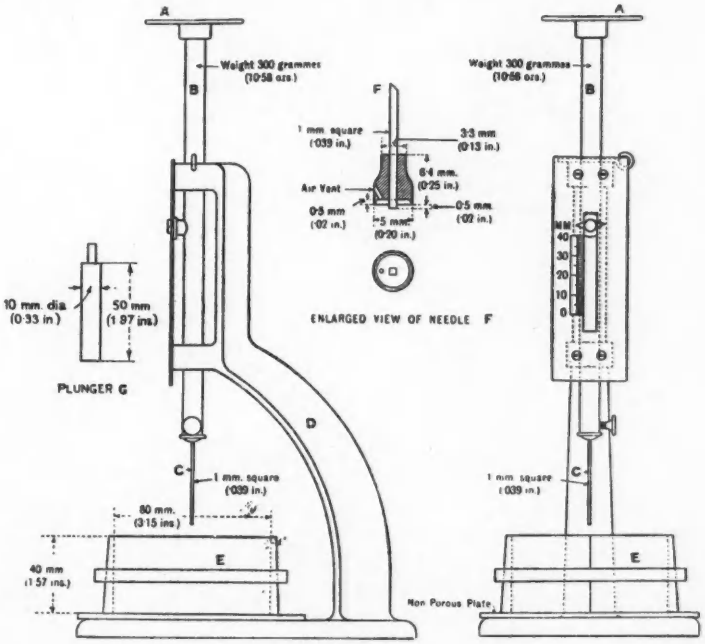


Fig. 2.

Two distinct stages of setting are recorded in the laboratory, *viz.*, the commencement of the setting (called the initial set), and the end, or final, set. With the Vicat type of needle, now so widely used for this test and standardised in Great Britain as well as in most foreign countries, the initial and final sets are readily observed, but the results must be interpreted somewhat broadly and are not precise to within minutes. Although the method chosen for testing the setting of cement may not give absolutely exact and precise results, it is satisfactory because one definite test has been adopted with well-defined conditions.

The method of applying a needle of a known weight and area has been adopted from the earliest times, and the British Standard Specification for Portland Cement requires that a needle of a type developed from that used by

Vicat and illustrated in Figs. 1 and 2 shall be used for testing the setting times. The methods for performing the test are described in the Specification as follows:

Tests for Setting Time.

Vicat Apparatus.—The initial and final setting times of the cement shall be determined by means of the Vicat apparatus.

For the purpose of carrying out the tests, a test block shall be made as follows: Neat cement shall be gauged in the manner and under the conditions referred to later. The test block shall be made by filling the cement, gauged as hereafter described, into the Vicat mould, the mould resting upon a non-porous plate. The mould shall be completely filled, and the surface of the paste shall then be smoothed off level with the top of the mould. Clean appliances shall be used for gauging, and the temperature of the water and that of the test room at the time when the operations are being performed shall be from 58 to 64 deg. Fahr. (14.4 to 17.8 deg. C.), subject to certain provisions for hot climates. The test block shall be kept during the whole time of the test in an atmosphere of at least 90 per cent. relative humidity and away from draughts.

Determination of Initial Setting Time.—For the determination of the initial setting time the test block confined in the mould and resting on the plate shall be placed under the rod bearing the needle; the latter shall then be lowered gently into contact with the surface of the test block and quickly released, and allowed to sink into it. This process shall be repeated until the needle, when brought into contact with the test block and released as described, does not pierce it completely. The period elapsing between the time when the water is added to the cement and the time at which the needle ceases to pierce the test block completely shall be the initial setting time.

Determination of Final Setting Time.—For the determination of the final setting time the needle of the Vicat apparatus shall be replaced by a needle with a ring attached. The cement shall be considered as finally set when, upon applying the needle gently to the surface of the test block, the needle makes an impression thereon while the attachment fails to do so. In the event of a scum forming on the surface of the test block, the underside of the test block may be used for determining the final set.

Fig. 2 is a diagrammatic illustration of the Vicat apparatus reproduced from the British Standard Specification for Portland Cement (1931), where it is described as follows, the figures in brackets being approximate equivalents:

The Vicat apparatus consists of a frame (D) bearing a movable rod (B) with at one end the cap (A), and at the other one of the following, which are removable: (*a*) The needle (C) for determining the initial setting time, (*b*) the needle (F) for determining the final setting time, or (*c*) the plunger (G) for determining the normal consistency. The needle (C) shall be 1 mm. (0.039 in.) square in section and have a flat end. The needle (F) shall be of the same shape and section as needle (C), but shall be fitted with a metal attachment hollowed out so as to leave a circular cutting edge 5 mm. (0.20 in.) in diameter, the end of the needle projecting 0.5 mm. (0.02 in.) beyond this edge. The plunger (G) shall be of polished brass 10 mm. (0.39 in.) in diameter, 50 mm. (1.97 in.) long, with a projection at the upper end for insertion into the movable rod (B), and the lower edge shall be flat. The movable rod (B) carries an indicator which moves over a graduated scale attached to the frame (D). With all attachments, the cap and rod, with needle (C) or needle (F), or plunger (G), shall together weigh 300 grammes (10.58 oz.). The mould for the cement consists of a split ring (E) 80 mm. (3.15 in.) in diameter, 40 mm. (1.75 in.) high, which rests on a non-porous plate.

It is prescribed that normal setting cement shall have an initial setting time of not less than thirty minutes and a final setting time of not more than ten hours. If a quick-setting cement is specified it must have an initial setting time of not less than five minutes and a final setting time of not more than thirty minutes.

It is well known that when the same cement is tested at different times and ages, even by the same operator, different percentages of water may be required to give the same plasticity, and widely different setting results may be shown. The use of a standard quantity of water for testing all cements in preparing the pat or sample for testing has not so far been considered practicable, and the procedure laid down in the B.S.S. is as follows:

Tests for Normal Consistency of Cement Paste.

For the purpose of arriving at the normal consistency of cement paste the Vicat apparatus is used, a plunger 1 cm. in diameter being employed. The quantity of water required to produce a paste of normal consistency is 0.78 of that required to give a paste which will permit of the settlement of the Vicat plunger to a point 5 to 7 mm. from the bottom of the Vicat mould when the cement paste is tested. The time of gauging, that is, the time elapsing from the moment of adding the water to the dry cement until commencing to fill the mould, must not be less than three minutes or more than five minutes. If a quick-setting cement has been specially specified or required, the time of gauging must not be less than two minutes or more than three minutes, and the filling of the mould must be completed within five minutes. In either case the gauging must be completed before signs of setting occur.

The cement paste is filled into the mould under the same conditions as for the setting-time test. In filling the mould the operator's hands and the blade of the ordinary gauging trowel alone may be used, and the trowel must weigh about 7½ oz. The mould, after being filled, may be lightly shaken to the extent necessary for expelling the air. The test-block confined in the mould and resting on the plate is placed under the rod bearing the plunger; the latter is then lowered gently into contact with the surface of the test-block, quickly released, and allowed to sink into it.

Trial pastes should be made with varying percentages of water until the amount necessary for determining the normal consistency, as defined, is found. This amount of water is recorded and expressed as a percentage by weight of the dry cement. This procedure is an improvement on that formerly adopted for ensuring agreement between different testers, but, even if the same percentage of water is used in mixing, differences in climatic conditions will cause the results of the setting-time test to vary considerably owing to the marked influence which temperature and energy of mixing have on setting.

Strict conditions must be observed in testing the activity of cements. One of these is referred to more particularly in an article bearing on the results of fine grinding (Cement and Cement Manufacture, February, 1932). Another very important factor is the temperature of the test-room, which has a serious influence on the speed of setting—high temperature or excess of CO_2 causing more rapid action. Generally speaking, both the initial and final periods of setting are prolonged by an increase of water in mixing, and the judgment of different observers is liable to make the test somewhat erratic and variable. In addition to ascertaining the setting times of cements, the variableness of the final hardening of different brands of cements is an important factor to be considered.

The reactions involved in the setting of cements have received much consideration by scientists for many years, but no method has yet been found to supersede that of adding calcium sulphate (usually in the form of raw gypsum)

to regulate the setting times. This was discussed at length in an earlier article (CEMENT AND CEMENT MANUFACTURE, August, 1931).

To regulate the setting of cement, a small percentage (generally about 2) of gypsum, a mineral with calcium sulphate as its essential constituent, and occurring in various parts of the country, is added to the cement during grinding, and generally does all that is necessary to slow down an inordinately quick-setting cement. The manufacturer, however, sometimes also has recourse to steam hydrating in the mills during the clinker-grinding operation, extensive "weathering" of the clinker before grinding, or the watering of the hot clinker when leaving the kilns or coolers. These methods of slowing the set have been used when the addition of gypsum was found to be insufficient by itself, and in combination have given dependable and satisfactory results on the whole.

Cement clinker, ground without gypsum directly it leaves the kiln, may set immediately water is added, and thereby become useless to the consumer. The introduction of gypsum during grinding, however, gives a cement which can be relied upon as being of a slow and generally uniform set. An absolute reliability of setting, however, cannot be assured, as occasionally cements which are slow-setting when freshly ground have been known to undergo temporary conversion to quick-setting on storage, and then again become slow. As a rule, cement will become slower-setting after storage, as a result of hydration of the calcium aluminate contained in it, the length and conditions of storage affecting the setting-time results very considerably.

By means of a microscope and with a magnification of about 200 it is possible to watch cement in the process of setting, and for this purpose a little cement should be dusted on to the slide and fastened down by a cover-glass, and both placed under water. It will then be noticed that the grains of cement become covered with crystals, which make their appearance sometimes in from ten to twenty minutes or sometimes from ten to fifteen hours according to the activity of the sample. These crystals are the result of the solution in the water of a portion of the cement, and their growth and interlocking on adjoining grains unite the whole into a solid mass and thus constitute the setting properties of cement. When once the crystals have formed they cannot be again dissolved, hence the weakness of cement which has been remixed after setting has taken place.

The test for setting of cements has much practical importance. It is direct so far as it prescribes the period within which the cement must be placed after mixing, and this period must not be longer than the time of initial set. It is indirect in so far as it relates to the probable final strength, elasticity, and hardness of the cement mixture.

A rough-and-ready form of testing setting time is to press the thumb-nail on a pat of cement and note the times of resistance to pressure. Thus, a small sample of cement is made up with about 25 per cent. of pure fresh water at normal temperature and formed on a piece of glass into a circular pat of about 3 in. in diameter by about $\frac{1}{4}$ in. thick. The initial and final setting times can then be very approximately ascertained by the impressions of the nail (or preferably by a pencil point) at varying intervals.

The accurate ascertaining of the setting time of Portland Cement is still a controversial point, and present methods are not entirely satisfactory. Whilst it is essential that a definite method of ascertaining and recording the final set and hardening should exist, it is probably of more importance to ascertain when the initial set of cement begins, for no user of cement can continue to mix or work cement after the initial set has commenced without risk of injury to the work upon which he is engaged.

As a corollary of the setting test it is necessary not only to measure the period required by the cement to acquire a determined set, as determined by the Vicat needle or by thumb pressure, but also to measure the hardness it has acquired after a determined time, as, for instance, the resistance to crushing or transverse strain in pounds per square inch. While it is necessary to know the initial setting time of a cement to avoid unsatisfactory consequences, it is also necessary to know its hardening properties which are of greater ultimate importance to the engineer and contractor. It will be observed that there is something more than the initial and final setting to be ascertained in testing the activity of Portland cement, and that is the period between the final set and the ultimate hardening of the product.

It may be said that the tensile and compression strength at three and seven days clearly denote the hardening properties of a cement. In testing at early dates, say, before three days, the ordinary testing machine puts an immediate

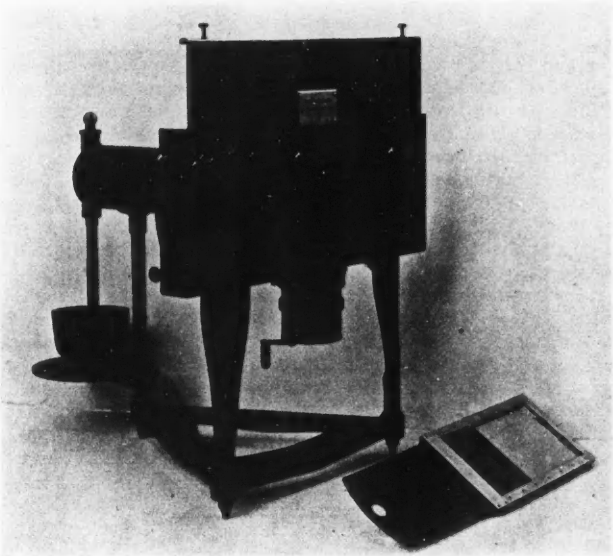


Fig. 3.

and proportionately heavy strain on the briquettes before the test starts. Because of this and the relatively large influence of humidity and temperature in the early stages of hardening, a 24- or 48-hour tensile or compression test may give erratic results, and very rigid conditions may have to be laid down for such a short-date test.

A test is required to gauge the hardening of cements at short intervals from the time of final set, and such a test must be applied with greater accuracy and care than is customary with the ordinary tensile test while still giving direct and quantitative information upon the hardening qualities of different cements at early dates, under precise conditions of humidity and temperature. A material

factor in the setting of cements could then be more carefully studied, and the results would be extremely valuable, especially with rapid hardening cements.

The variable results reported in the early hardening of cements—a point of considerable importance to the constructional engineer and contractor—show the necessity of such a test having in view a more careful study of the rapid hardening cements increasingly employed at the present time.

It is important that setting should be as slow as possible, but limits are put to this by the contrary need for considerable strength in a short time. Neither the ordinary initial nor final setting test gives this information, and whereas most cements show initial and final sets within reasonable limits they may harden at periods varying from some hours to days.

It has been proposed from time to time that a test which would measure the rise of temperature during the setting of cement should be carried out as a means of determining the set or hardening. Such a test may be made by applying a small thermometer to the block of cement when freshly mixed and placed in, say, the Vicat mould as used for the setting test. Upon the insertion of the thermometer into the plastic cement the temperature is taken and noted, and it will be observed that the temperature during setting slowly rises until hardening has commenced in the cement under test. The highest point of temperature, before the mercury descends, should be noted, as should also the time of the insertion of the thermometer and the time of the completion of the test. More than one apparatus has been devised for automatically recording the results both by an ordinary recording chart and photographically, an example of the latter being illustrated in Fig. 3. The advantage of this test over the needle has not been generally accepted and its variations have not been fully explained, nor indeed can information of practical value be said to be obtained from the results. It is reasonable to assume, however, that the quicker setting cements show an increased temperature during the setting, taking into account the period during which heat is evolved. For example, with cement of great initial activity (*i.e.*, cement of quick setting properties) the heat is developed in a short period and consequently shows itself in a rise in temperature. With slower setting cement the evolution of the same amount of heat would be spread over several hours, and in consequence would not be so noticeable owing to relatively greater radiation. The temperature of cement in setting is therefore, perhaps, more an index as to the setting of the cement than to its hardening qualities.

Cement Production in Russia.

The following figures are given to illustrate the increase that has taken place in cement production in Russia during the past four years, but should be accepted with a certain amount of reserve: 1928, 1,833,000 tons; 1929, 2,333,000 tons; 1930, 3,333,000 tons; 1931, 3,583,000 tons. According to the Five Years Plan production in 1932 should reach 5,000,000 tons.

Australian Cement, Ltd.

Australian Cement, Ltd., has declared a dividend of 10 per cent. for the year ending November, 1931, with a net profit of £46,406. This compares with a dividend of 11½ per cent. for 1930 and a net profit of £45,557. The chairman stated in his report for last year that the company had had the lowest turnover since 1920. There were, however, definite signs of improvement in the building trade in 1932.

Synthesis of Calcium Silicates.

THE results of researches on calcium silicate undertaken by Professor Shoichiro Nagai and Professor Kei-ichi Akiyama, of the Applied Chemistry Department of the Tokyo Imperial University, were published in the "Journal" of the Society of Chemical Industry, Japan, recently. These investigations on the synthesis of calcium silicate were studied on the same principles as those of Le Chatelier, Jaenecke, Nacken, Newberry, Dyckerhoff, and others, and the preparations were made by high-temperature methods so that the results can be compared with previous investigations of similar compounds obtained by reaction in the presence of water.

Pure calcium carbonate and silicic acid anhydride were mixed in the molecular relation 1 : 1, and this mixture is denoted as $CaCO_3 : SiO_2(1 : 1)$, hereafter. The mixture was heated at various temperatures between 900 deg. C. and 1,550 deg. C., or higher temperatures, for one hour, and the heated products were tested for free lime, combined lime, insoluble or uncombined silica, combined or soluble silica, specific gravity, etc. By the calculation of the molecular ratio of combined lime to combined silica the kind of calcium silicates produced in each heated sample was determined. The results are shown in Table 1.

TABLE I.

RESULTS OF SYNTHESIS OF CALCIUM SILICATES FROM MIXTURE $CaCO_3 : SiO_2(1 : 1)$.

Experiment No.	Heating temp. deg. C.	Heating time, hours.	Per cent. of Comb. CaO to		Per cent. of Comb. SiO_2 to		Total Calcium Silicates, per cent.	Molecular Ratio of Comb. CaO to Comb. SiO_2	Specific Gravity
			Sample.	Total CaO.	Sample.	Total SiO_2.		$CaO : SiO_2$	
101	900	1	11.83	24.50	8.93	17.30	20.79	1.41 : 1.00	2.50
102	1,000	1	16.83	34.86	12.04	23.28	28.87	1.50 : 1.00	2.71
103	1,100	1	19.08	39.52	12.84	24.83	31.92	1.59 : 1.00	2.75
104	1,200	1	28.55	59.13	16.83	32.54	45.38	1.82 : 1.00	2.78
105	1,300	1	38.58	79.91	22.11	42.77	60.69	1.87 : 1.00	2.86
106	1,400	1	43.50	90.10	27.16	52.51	70.66	1.94 : 1.00	2.90
107	1,450	1	48.28	1.00	43.54	84.18	91.82	1.19 : 1.00	2.82
108	1,500	1	48.28	1.00	48.05	92.90	96.33	1.07 : 1.00	2.82
109	1,550	1	48.28	1.00	46.60	90.10	94.88	1.11 : 1.00	2.83

It will be seen that $3CaO.2SiO_2$ was first produced by heating at between 900 deg. C. to 1,100 deg. C., and was gradually changed to $2CaO.SiO_2$ at 1,200 deg. C. to 1,400 deg. C. It was again changed to $CaO.SiO_2$ by heating at 1,450 deg. C. or higher temperatures (1,500 deg. C. or 1,550 deg. C.), which are close to the melting point (1,540 deg. C.) of $CaO.SiO_2$. Lime was completely combined at 1,450 deg. C., but silica was not completely combined by heating even at 1,500 or 1,550 deg. C., which shows that one hour of heating is too short for complete combination. Thus it is necessary to heat the sample for longer periods to obtain the complete combination of silica and lime to pure $CaO.SiO_2$, as was proved by experiment No. 110.

$CaO.SiO_2$ was obtained by experiment No. 110, as shown in Table II.

This sample was used to test the hydraulic properties of $CaO.SiO_2$, and it was clearly ascertained that $CaO.SiO_2$ has very weak hydraulic properties compared with those of calcium aluminates, but the hydraulic strength increased very slowly by long ageing in water.

TABLE II.

$CaO.SiO_2$ OBTAINED BY HEATING AT 1,300 DEG. C. FOR 5 HOURS.

Experiment No.	Heating temp. deg. C.	Heating time, hours.	Per cent. of Comb. CaO to		Per cent. of Comb. SiO_2 to		Total Calcium Silicates, per cent.	Molecular Ratio of Comb. CaO to Comb. SiO_2	Specific Gravity
			Sample.	Total CaO.	Sample.	Total SiO_2.		$CaO : SiO_2$.	
110	1,300	5	48.28	100	47.28	91.42	95.56	1.09 : 1.00	2.81

Results of tests on the high-temperature synthesis of dicalcium silicate $2CaO.SiO_2$ and its hydraulic strengths are next described. Small test pieces of 1 : 3 mortar were used.

Pure calcium carbonate and silicic acid anhydride were mixed in the molecular relation 2 : 1, which is denoted as $2CaCO_3 : SiO_2$, or $2CaO : SiO_2$ after calcining. The mixture was heated at several temperatures from 900 deg. C. to 1,550 deg. C. or higher for one hour, and the heated products were tested. By calculating the percentages of combined lime to total lime, combined silica to total silica, and the total amount of calcium silicates produced (the sum of the combined lime and silica), the conditions of combination between lime and silica were investigated. The most important factors are the values of specific gravities and molecular ratios of combined lime to combined silica. By a comparison of these data the kind of calcium silicates produced in each of the heated samples was determined. These results are shown in Table III.

TABLE III.

RESULTS OF SYNTHESIS OF CALCIUM SILICATES FROM MIXTURE $2CaCO_3 : SiO_2(2 : 1)$.

Experiment No.	Heating temp. deg. C.	Heating time, hours.	Per cent. of Comb. CaO to		Per cent. of Comb. SiO_2 to		Total Calcium Silicates, per cent.	Molecular Ratio of Comb. CaO to Comb. SiO_2	Specific Gravity
			Sample.	Total CaO.	Sample.	Total SiO_2.		$CaO : SiO_2$.	
201	900	1	8.47	13.01	6.36	18.23	14.83	1.43 : 1.00	2.72
202	1,000	1	12.15	18.66	8.11	23.25	20.26	1.61 : 1.00	2.78
203	1,100	1	16.05	24.65	9.60	27.52	25.65	1.79 : 1.00	2.82
204	1,200	1	28.52	43.80	15.20	43.58	43.72	2.02 : 1.00	2.96
205	1,300	1	34.21	52.53	18.54	53.15	52.75	1.98 : 1.00	2.90
206	1,400	1	42.39	65.10	22.95	65.79	65.34	1.98 : 1.00	2.86
207	1,450	1	64.42	98.93	34.80	99.77	99.22	1.98 : 1.00	3.06
208	1,500	1	64.73	99.41	30.53	87.53	95.26	2.26 : 1.00	2.88
209	1,550	1	62.74	96.35	28.01	80.30	90.75	2.40 : 1.00	2.93

It will be seen from these results that part of the $3CaO.2SiO_2$ was first produced by heating at between 900 deg. C. and 1,000 deg. C., and was gradually changed to $2CaO.SiO_2$ at 1,100 deg. C. and 1,200 deg. C. The products heated at 1,200 deg. C. and higher temperatures had molecular ratios of combined lime to combined silica equal to nearly 2. The total of calcium silicates produced became gradually greater, from 15 per cent. (No. 201) to ca. 65 per cent. (No. 206) at 1,400 deg. C., but at 1,450 deg. C. it increased rapidly to nearly 99 per cent. At 1,500 deg. C. and 1,550 deg. C. there were smaller amounts of calcium silicates (90 to 95 per cent.), but their molecular ratios of combined lime to combined silica were greater (2.26 to 2.40) than 2, showing that a little $3CaO.SiO_2$ had already been

produced. The samples heated at 1,400 deg. C. and higher temperatures disintegrated, without exception, to powder on cooling. This fact shows that α-$2CaO.SiO_2$ or β-$2CaO.SiO_2$ transformed to γ-$2CaO.SiO_2$, which coincides strictly with the low values of specific gravities.

Slightly larger amounts of $2CaO.SiO_2$ were produced by applying these results. The products were analysed with the results shown in Table IV.

TABLE IV.

$2CaO.SiO_2$ FOR TESTING HYDRAULIC STRENGTH OF MORTAR BY SMALL-PIECE TESTING METHOD.

Experiment No.	Heating temp. deg. C.	Heating time, hours.	Combined CaO, per cent.	Free CaO, per cent.	Combined SiO_2, per cent.	Free SiO_2, per cent.	Total Calcium Silicates, per cent.	Molecular Ratio of Comb. CaO to Comb. SiO_2 CaO : SiO_2.	Specific Gravity
210	1,200	30	55.84	9.28	28.88	5.77	84.72	2.07 : 1.00	3.04
211	1,450	5	65.12	0	34.71	0.16	99.88	2.01 : 1.00	3.02
212	1,300	2	63.71	1.41	34.66	0.21	98.37	1.97 : 1.00	3.24
213	1,450	1	64.85	0.27	34.81	0.02	99.71	2.00 : 1.00	3.20
214	1,450	1	65.12	0	34.65	0.13	99.77	2.01 : 1.00	3.22

A small amount of borax was used as a flux in samples No. 212 (borax 1 per cent.), No. 213 (borax 3 per cent.), and No. 214 (borax 4 per cent.). No. 210 did not combine completely, even by heating for 30 hours, and contained 15 per cent. of free lime and silica owing to the low temperature (1,200 deg. C.). No. 211 disintegrated, but Nos. 212, 213, and 214 did not disintegrate (due to the small amount of borax) and their high specific gravities.

Samples Nos. 211, 212, and 214 were used to study the hydraulic properties of $2CaO.SiO_2$, and the strength of 1 : 3 mortar. The small-piece testing method, which was proposed by one of the authors and used in the studies on calcium aluminates, calcium ferrites, etc., was adopted. The results are given in Table V, in which $CaO.SiO_2$ is compared.

TABLE V.

STRENGTH TESTS OF $2CaO.SiO_2$ AND $CaO.SiO_2$ BY 1 : 3-MORTAR SMALL-PIECE TESTING METHOD.

Experiment No.	Water-Cement Ratio, per cent.	Compressive Strength (kg./cm.²) tested by Small Cylindrical Test Piece (dia. 2 cm., length 3 cm.).					
		3 days.	7 days.	28 days.	Comb. 28 days.	56 days.	Comb. 56 days
110	65	2.1	3.3	6.0	6.1	—	—
211	65	3.5	9.6	24.2	24.6	—	—
212	60	3.3	14.8	25.6	26.8	24.6	33.9
214	60	3.1	7.9	11.4	17.2	14.6	20.6

The test pieces were cured in moist air. In the combined curing the test pieces were immersed in water after 7 days curing in moist air. No. 110, $CaO.SiO_2$, had very poor strength. Nos. 211 and 212 showed a little better results, but No. 214 had less strength, due to the addition of too much borax (4 per cent.). The strength of $2CaO.SiO_2$ slowly increased at 28 and 56 days in water curing. But these strengths of calcium silicates are poor compared with those of calcium aluminates tested by the author.

The results of studies on thermal synthesis of tricalcium silicate $3CaO.SiO_2$ from (1) the mixture $3CaO : SiO_2$(3 : 1) composed of $CaCO_3$ and SiO_2 and (2) from the mixture $x(3CaO : SiO_2) + y(2CaO : Fe_2O_3)$ composed of $CaCO_3$, SiO_2, and Fe_2O_3 were as follows:

For the first mixture, $3CaO : SiO_2$, pure calcium carbonate and silicic acid anhydride were mixed in the molecular ratio 3 : 1, denoted as $3CaCO_3 : SiO_2$ or $3CaO : SiO_2$. For the second mixture, pure calcium carbonate, silicic acid anhydride and ferric oxide were mixed in the molecular ratios (a) 3 : 1 in $3CaCO_3 : SiO_2$ or $3CaO : SiO_2$ and (b) 2 : 1 in $2CaCO_3 : Fe_2O_3$ or $2CaO : Fe_2O_3$. The mixing ratio was 80 to 95 per cent. of (a) and 20 to 25 per cent. of (b).

The first mixture of the two-component system $CaO–SiO_2$($3CaO : SiO_2$) was heated at several temperatures ranging from 900 deg. C. to 1,600 deg. C. for one hour by the same heating method and apparatus used in the previous tests and in one case by oxygen-coal gas flame. The second mixture of the three-component system $CaO–SiO_2–Fe_2O_3$ $[x(3CaO : SiO_2) + y(2CaO : Fe_2O_3)]$ was heated at 1,450 deg. C. for periods of from 1 to 8 hours.

The heated products were tested for free lime, combined lime, uncombined or insoluble silica, combined or soluble silica, specific gravity, etc. From these data, calculating the percentages of combined lime to total lime, combined silica to total silica, and the total amount of calcium silicates produced, information was sought on the conditions of combination between lime and silica.

The most important factor is the change in the value of molecular ratio of combined lime to combined silica, this being the molecular ratio of lime to silica of the calcium silicate produced, and showing the type of silicates produced during heating. The results are given in Table VI.

TABLE VI.

RESULTS OF THERMAL SYNTHESIS OF CALCIUM SILICATES FROM MIXTURE $3CaCO_3 : SiO_2$(3 : 1).

Experiment No.	Heating temp. deg. C.	Heating time, hours.	Per cent. of Comb. CaO to		Per cent. of Comb. SiO_2 to		Total Calcium Silicates, per cent.	Molecular Ratio of Comb. CaO to Comb. SiO_2	Specific Gravity
			Sample.	Total CaO.	Sample.	Total SiO_2.		CaO : SiO_2.	
301	900	1	10.20	13.34	9.53	36.22	19.73	1.15 : 1.00	2.99
302	1,000	1	10.69	14.51	9.68	36.80	20.37	1.18 : 1.00	2.98
303	1,100	1	16.74	22.72	14.21	54.00	30.95	1.26 : 1.00	3.08
304	1,200	1	37.76	51.24	21.50	81.70	59.26	1.88 : 1.00	3.14
305	1,300	1	45.42	61.64	24.98	94.97	70.40	1.95 : 1.00	3.16
306	1,400	1	49.01	66.51	26.19	99.52	75.20	2.00 : 1.00	3.09
307	1,500	1	49.07	66.60	26.22	99.61	75.29	2.00 : 1.00	3.06
308	1,600	1	52.96	71.98	26.22	99.61	79.18	2.16 : 1.00	3.13
309	Oxygen-gas flame	coal	51.32	69.65	25.81	98.08	77.13	2.13 : 1.00	3.05

It will be seen from these results that 60 to 70 per cent. $2CaO.SiO_2$ was produced at 1,200 to 1,300 deg. C. These percentages are greater than those in the case of heating the mixture $2CaCO_3 : SiO_2$(2 : 1), and is due to the high lime content. The products heated at 1,200 deg. C. and higher temperatures had molecular ratios of combined lime to combined silica of nearly 2.0 of the dicalcium silicate $2CaO.SiO_2$. The heated products at 1,600 deg. C. or by oxygen-coal gas flame had slightly higher molecular ratios than 2.0, showing that a small amount of $3CaO.SiO_2$ was produced. The products heated at 1,400 deg. C. or

higher temperatures disintegrated to powder on cooling. This is due to the transformation of tricalcium silicate $3CaO.SiO_2$ to dicalcium silicate $2CaO.SiO_2$ and free lime CaO, and α- or β-form of this dicalcium silicate to γ-form, which coincide well with the small values of molecular ratios of combined lime to combined silica and specific gravities.

From these results it is clear that $3CaO.SiO_2$ cannot be easily obtained by only heating the single mixture $3CaCO_3 : SiO_2$(3 : 1) for one hour or so up to 1,500 deg. C. to 1,600 deg. C. It may be obtained by heating at higher temperatures for longer periods or by repeated heating.

The authors have studied the combination between CaO and SiO_2 in the presence of a small amount of Fe_2O_3 and Al_2O_3, or both. In the case of a high lime mixture $2CaO.Fe_2O_3$ dicalcium ferrite is the highest lime content product, which is easily obtained by heating at about 1,400 deg. C. The second mixtures of 80 to 95 per cent. $3CaCO_3 : SiO_3$ and 20 to 25 per cent. $2CaCO_3 : Fe_2O_3$ were heated at 1,450 deg. C. for 1, 2, 4, and 8 hours. The heated products were examined for their free and combined lime, uncombined and combined silica, ferric oxide, etc., as in the previous tests. The molecular ratio of combined lime to combined silica and the combination to $3CaO.SiO_2$ is shown in Table VII.

TABLE VII.

RESULTS OF THERMAL SYNTHESIS OF CALCIUM SILICATES FROM MIXTURES $x(3CaCO_3 : SiO_2) + y(2CaCO_3 : Fe_2O_3)$. (HEATING TO 1,450 DEG. C.)

Experiment No.	Mixing Ratios of Raw Materials in					Heating time, hours.	Free Lime in		Molecular Ratio of Comb. CaO to Comb. SiO_2
	Components.			Proportion.			Sample.	Total Silicates,	
	CaO per cent.	SiO_2 per cent.	Fe_2O_3 per cent.	$3CaO : SiO_2$ per cent.	$2CaO : Fe_2O_3$ per cent.		per cent.	per cent.	$CaO : SiO_2$
210	67.02	21.05	11.75	80	20	4	4.01	5.01	2.79 : 1.00
311	70.44	23.68	5.88	90	10	4	8.34	9.27	2.63 : 1.00
312	72.08	24.98	2.94	95	5	4	8.04	8.47	2.66 : 1.00
313	72.08	24.98	2.94	95	5	1	11.92	12.54	2.48 : 1.00
314	72.08	24.98	2.94	95	5	2	6.70	7.06	2.71 : 1.00
315	72.08	24.98	2.94	95	5	4	6.68	7.03	2.71 : 1.00
316	72.08	24.98	2.94	95	5	8	6.70	7.06	2.71 : 1.00

It is shown that $3CaO.SiO_2$ is easily obtained by the presence of a small amount of Fe_2O_3 of $2CaO.Fe_2O_3$, which can be completely formed by heating at about 1,400 deg. C. for one to two hours and melted at 1,450 deg. C. to react as a fluxing agent to the formation of $3CaO.SiO_2$. The molecular ratio of combined lime to combined silica in the silicates produced is about 2.6 to 2.7, which shows that nearly 60 to 70 per cent. of $3CaO.SiO_2$ is contained in the total silicate mixture. The ratio became gradually higher in the high ferric oxide mixture or by longer heating to eight hours.

The results of studies on the thermal synthesis of calcium silicates between CaO and SiO_2 in the presence of (1) Al_2O_3 as $CaO–SiO_2–Al_2O_3$ ternary system and (2) Al_2O_3 and Fe_2O_3 as $CaO-SiO_2-Al_2O_3-Fe_2O_3$ quaternary system were as follows.

For the first mixture of the ternary system, pure calcium carbonate, silicic acid anhydride, and aluminium oxide were mixed in the molecular proportions (a) 3 : 1 in $3CaCO_3 : SiO_2$ or $3CaO : SiO_2$ and (b) 3 : 1 in $3CaCO_3 : Al_2O_3$ or

$3CaO : Al_2O_3$. The mixing ratios were (a) $3CaO : SiO_2$ in 70, 80, 90 and 95 per cent., and (b) $3\,CaO : Al_2O_3$ in 30, 20, 10 and 5 per cent by weight, as shown in Table VIII.

TABLE VIII.

PROPORTIONS OF TERNARY MIXTURES ($CaO–Si_2O–Al_2O_3$) AND FREE LIME IN HEATED PRODUCTS.

Experiment No.	Mixing Ratios of Raw Materials in Component.			Mixing Ratios of Raw Materials in Proportion.		Free Lime in	
	CaO per cent.	SiO_2 per cent.	Al_2O_3 per cent.	$3CaO : SiO_2$ per cent.	$3CaO : Al_2O_3$ per cent.	Heated Products, per cent.	Total Silicate, per cent.
317	70.25	18.42	11.33	70	30	5.71	8.16
318	71.39	21.05	7.56	80	20	7.25	9.07
319	72.54	23.68	3.78	90	10	8.68	9.64
320	73.13	24.98	1.89	95	5	16.52	17.39

For the second mixture of the quaternary system, the three raw materials and ferric oxide were mixed in the molecular ratios (a) 3 : 1 in $3CaCO_3 : SiO_2$ or $3CaO : SiO_2$, (b) 3 : 1 in $3CaCO_3 : Al_2O_3$ or $3CaO : Al_2O_3$, and (c) 2 : 1 in $2CaCO_3 : Fe_2O_3$, or $3CaO : Fe_2O_3$. The mixing ratios were (a) $3CaO : SiO_2$, 75 to 80 per cent.; (b) $3CaO : Al_2O_3$, 15 to 20 per cent.; (c) $2CaO : Fe_2O_3$, 5 to 7 per cent. by weight, as shown in Table IX.

TABLE IX.

PROPORTIONS OF QUATERNARY MIXTURES ($CaO–SiO_2–Al_2O_3–Fe_2O_3$) AND FREE LIME IN HEATED PRODUCTS.

Experiment No.	Mixing Ratios of Raw Materials in Component.				Mixing Ratios of Raw Materials in Proportion.				Free Lime in	
	CaO per cent.	SiO_2 per cent.	Al_2O_3 per cent.	Fe_2O_3 per cent.	$3CaO : SiO_2$ per cent.	$2CaO : SiO_2$ per cent.	$3CaO : Al_2O_3$ per cent.	$2CaO : Fe_2O_3$ per cent.	Heated Product, per cent.	Total Silicate, per cent.
321	70.34	21.05	5.67	2.94	80	—	15	5	5.94	7.42
322	67.91	22.48	5.67	2.94	63.2	16.8	15	5	0	0
323	70.34	21.05	5.67	2.94	80	—	15	5	6.62	8.27
324	70.34	21.05	5.67	2.94	80	—	15	5	4.68	5.85
325	69.78	19.73	7.54	2.94	75	—	20	5	3.64	5.22
326	69.36	19.73	6.79	4.11	75	—	18	7	3.15	4.53

These two mixtures were heated at 1,450 deg. C. for four hours and the heated products analysed in the same way as in the previous tests for insoluble residue, soluble silica, alumina and ferric oxide, total lime, free lime, etc. In no case was there any insoluble residue, showing that all silica, alumina and ferric oxide were completely combined with calcium oxide to soluble silicates, aluminate and ferrite. At this high temperature and long heating in the presence of excess lime to alumina or ferric oxide, the aluminate and ferrite became the compounds of highest lime content, i.e., $3CaO.Al_2O_3$ and $2CaO.Fe_2O_3$.

From these data the amounts of $3CaO.Al_2O_3$, $3CaO.SiO_2$, $2CaO.SiO_2$, and the molecular ratio of combined CaO to combined SiO_2 were calculated as shown in Table X.

TABLE X.

RESULTS OF THERMAL SYNTHESIS OF CALCIUM SILICATES FROM MIXTURES OF CaO–SiO_2–Al_2O_3 TERNARY SYSTEM.

(HEATING TO 1,450 DEG. C. FOR 4 HOURS.)

Experiment No.	Compound.			Molecular Ratio of Comb. CaO to Comb. SiO_2	Ratio of $3CaO.SiO_2$ to $2CaO.SiO_2$
	$3CaO.Al_2O_3$ per cent.	$3CaO.SiO_2$ per cent.	$2CaO.SiO_2$ per cent.	$CaO : SiO_2$	
317	30.02	46.80	17.62	2.67 : 1.00	2.66
318	20.03	50.85	21.99	2.63 : 1.00	2.31
319	10.00	54.75	26.73	2.60 : 1.00	2.05
320	5.01	28.00	50.67	2.30 : 1.00	0.55

From these results it is seen that the percentages of produced $3CaO.SiO_2$ and $2CaO.SiO_2$, and the ratios between these two silicates, were proportional to the amount of Al_2O_3 or $3CaO.Al_2O_3$. Thus the presence of Al_2O_3 or $3CaO.Al_2O_3$ is a necessary condition for the formation of $3CaO.SiO_2$ in the heating of Portland cement clinker. But this effect of Al_2O_3 is much less than that of Fe_2O_3

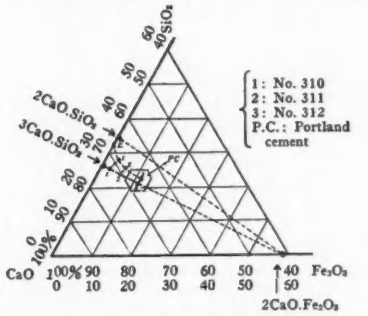


Fig. 1.—$CaO-SiO_2-Fe_2O_3$. Three Components Diagram.

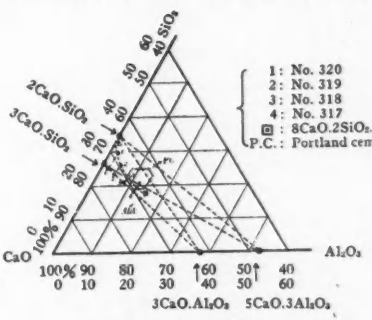


Fig. 2.—$CaO-SiO_2-Al_2O_3$. Three Components Diagram.

in the previous tests. These effects of Al_2O_3 and Fe_2O_3 and the relative effect of these sesqui-oxides are more clearly seen by the ternary diagrams (Figs. 1 and 2).

Table XI was obtained from the heated products in Table IX.

TABLE XI.

RESULTS OF THERMAL SYNTHESIS OF CALCIUM SILICATES FROM MIXTURES OF CaO–SiO_2–Al_2O_3–Fe_2O_3 QUATERNARY SYSTEM.

(HEATING AT 1,450 DEG. C. AND 4 HOURS.)

Experiment No.	Compound.				Molecular Ratio of Comb. CaO to Comb. SiO_2	Ratio of $3CaO.SiO_2$ to $2CaO.SiO_2$
	$3CaO.Al_2O_3$ per cent.	$2CaO.Fe_2O_3$ per cent.	$3CaO.SiO_2$ per cent.	$2CaO.SiO_2$ per cent.	$CaO : SiO_2$	
321	15.02	5.00	55.84	18.36	2.70 : 1.00	3.04
322	15.02	5.00	63.36	16.79	2.70 : 1.00	3.78
323	15.02	5.00	53.07	20.45	2.67 : 1.00	2.60
324	15.02	5.00	60.98	14.48	2.76 : 1.00	4.21
325	19.98	5.00	60.44	11.09	2.80 : 1.00	5.45
326	17.99	6.99	62.36	9.64	2.83 : 1.00	6.47

From these results is seen that the molecular ratio of combined CaO to combined SiO_2 in calcium silicates became gradually greater in proportion to the amounts of Al_2O_3 and Fe_2O_3 or $3CaO.Al_2O_3$ and $2CaO.Fe_2O_3$. But the free lime still remained even in the mixtures Nos. 325 and 326, in which Al_2O_3 and Fe_2O_3 were mixed in larger proportions than in No. 321. Nos. 323

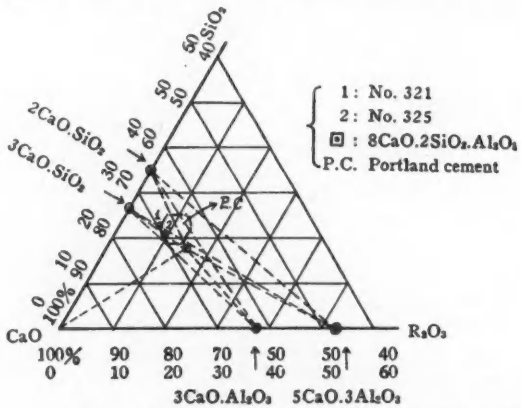


Fig. 3.—CaO—SiO_2—R_2O_3, Ternary System.

and 324 were examined by adding 1 per cent. of MgO or Cr_2O_3 to No. 321. No. 322 was tested by subtracting about 6 per cent. of lime from No. 321, and resulted in the sample containing no free lime. The molecular ratio of combined CaO to combined SiO_2 was to 2.70, and higher ratio of $3CaO.SiO_2$ to $2CaO.SiO_2$ than that of No. 321.

The ternary systems CaO–SiO_2–Fe_2O_3 in the previous tests and CaO–SiO_2–Al_2O_3 in the now considered paper were plotted on the ternary diagrams Figs. 1 and 2. The points of original mixtures were on the line of

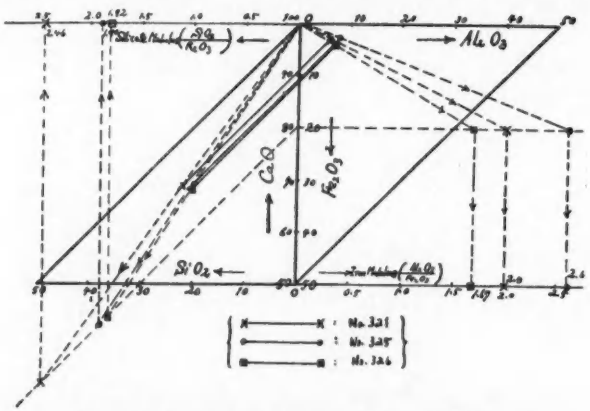


Fig. 4.—CaO—SiO_2—Al_2O_3—Fe_2O_3 Parallelogram.

$3CaO.SiO_2$–$2CaO.Fe_2O_3$ (Fig. 1) or $3CaO.SiO_2$–$3CaO.Al_2O_3$ (Fig. 2). These points were moved in the directions shown by the arrows to the points, which can be calculated from the results in the Tables X and XI by subtracting the free lime. These latter points are nearer to the line of $3CaO.SiO_2$–$2CaO.Fe_2O_3$ (Fig. 1) or $2CaO.SiO_2$–$3CaO.Al_2O_3$ (Fig. 2) than the former points. These diagrams show very clearly the fact that $3CaO.SiO_2$ can be obtained in the presence of Al_2O_3 and Fe_2O_3, or of both. These removed points are on the curve connecting the points E (the eutectic point of $3CaO.SiO_2$ and $2CaO.SiO_2$) and $8CaO.2SiO_2.Al_2O_3$ (Alit).

For the quaternary system the parallelogram (Fig. 4) was applied. On calculating Fe_2O_3 by $0.42 \times Fe_2O_3$ and adding to Al_2O_3, the ternary system (CaO–SiO_2–R_2O_3) was plotted in the ternary diagram (Fig. 3).

Cement Companies' Dividends and Reports.

German Cement Companies' Reports.

Anneliese Portland-Cement-und-Wasserkalk A.G. has declared a dividend of 10 per cent. for the year 1931, with a net profit of RM. 251,624 (£12,581). This compares with a dividend of 12 per cent. and a net profit of RM. 259,452 (£12,972) in 1930.

Vorwohler Portland-Cement-Fabrik passed its dividend for the year 1931; there was a gross loss of RM. 100,000. A dividend of 6 per cent. was paid for 1930, when the gross profit was RM. 82,851 (£4,142).

Bonner Bergwerks-und-Hutten Verein A.G. (associated with Dyckerhoff) passed its dividend for the year 1931, as it did for 1930. The gross loss in 1931 was RM. 550,791 (£27,539) while in 1930 there was a gross profit of RM. 206,470 (£10,323).

Belgian Cement Companies' Dividends.

"Cannon" Brand Artificial Portland Cement Works Co., Ltd., has declared a dividend of 5 per cent. for the year 1931, with a net profit of 4,188,422 francs (£23,933). A dividend of 5 per cent. was also paid in 1930 when the net profit was 3,112,628 francs (£17,786).

S.A. Des Ciments de Thieu has passed its dividend for the year 1931. A dividend of 5 per cent. was paid for the year 1930.

Ciments d'Oburg S.A. made a net profit of 2,764,000 francs (£15,794) in 1931, which compares with a net profit of 3,880,429 francs (£22,173) in 1930.

Ciments de Haren reports a profit of 989,019 francs (£5,651) for 1931, compared with 514,021 francs (£2,937) for 1930.

Ciments Portland Artificiels de Buda passed its dividend for 1931; the net profit was 546,791 francs (£3,124). A dividend of 50.60 francs net was paid in 1930, when the net profit was 565,073 (£3,228).

S.A. des Usines Levie Freres, Cronfestu, reports a net profit of 800,450 francs (£4,574) for the year 1931; no dividend is declared.

S.A. Niel-on-Rupel shows a profit of 3,898,356 francs (£22,276) for 1931, which compares with 4,044,025 francs (£23,108) for 1930.

Ciments de Vise has declared an ordinary dividend of 78 francs net for the year 1931, with a net profit of 1,363,638 francs (£7,792). The same dividend was paid in 1930, when the net profit was 1,039,529 francs (£5,940).

Kandos Cement Co., Ltd.

The board has decided not to pay an interim dividend for the half-year ended December 31 last, although the half-year's operations resulted in a profit.

United States Companies' Reports.

Alpha Portland Cement Company reports a net loss of 778,951 dollars (£160,270) for the year 1931, against a net profit of 1,248,853 dollars (£256,965) for 1930.

North American Cement Corporation made a net loss of 496,520 dollars (£102,164) for 1931, compared with a net profit of 263,092 dollars (£54,134) in 1930.

International Cement Corporation reports a net profit of 1,433,129 dollars (£294,882) for the year 1931, compared with a net profit of 4,538,509 dollars (£933,849) for 1930.

Egyptian Cement Company.

Societe Egyptienne de Ciment Portland Tourah reports a net loss of £E11,740 in 1931, when a loss of £E31,470 was incurred through depreciation of the pound sterling. This compares with a net profit of £E2,290 in 1930. It has been decided to close down the cement works at Massarah and to concentrate production at the company's works at Tourah. A third kiln is being installed with an annual capacity of 130,000 tons, and it is hoped to place this kiln into operation by the summer of 1932, thus making the total output of the Tourah works 250,000 tons per annum.

French Company's Dividends.

S.A. des Chaux et Ciments Portland du Haut-Rhin, Altkirch, has declared a dividend of 12 per cent. for the year 1931, with a net profit of 4,010,000 francs (£32,284). This compares with a dividend of 15 per cent. and a net profit of 3,487,260 francs (£28,075) for 1930.

S.A. des Ciments de Mantes showed a loss of 5,423,283 francs (£43,662) for the year 1931, against a loss of 375,142 francs (£2,920) for 1930.

The Canada Cement Co., Ltd.

The Canada Cement Co., Ltd., reports a profit of 1,553,191 dollars, equal to 32 cents on its Common shares, for the year 1931, compared with a net profit of 1,566,014 dollars for 1930, equal to a dividend of 33 cents. The plants of this company were working at approximately 60 per cent. of their capacity during 1931.

Rumanian Cement Company's Dividend.

S.A. de Cementuri din Europa Orientala has declared a net dividend of 13 per cent. for the year 1931, with a net profit of 3,273,128 francs (£18,700). This compares with a dividend of 17 per cent. and a net profit of 4,570,363 francs (£26,116) for 1930.

Italian Cement Company's Loss.

L'Unione Italiana Cementi, Casale Monferrato, reports a loss of L.4,416,623 (£47,767) for 1931.

Luxembourg Cement Company's Dividend.

S.A. des Ciments Luxembourgeois has declared a dividend of 10 per cent. for 1931, with a net profit of 736,842 francs (£4,210). This compares with a dividend of 15 per cent. for 1930, when the net profit was 1,176,315 francs (£6,721).

Dutch Cement Company's Report.

Soc. Erste Nederlandische Cement Industries reports a net profit of Fl. 598,000 (£49,380) for 1931, which compares with Fl. 602,689 (£49,767) for 1930.

Research on Portland Cement by means of Vapour Pressure Measurements.

By F. KRAUSS and W. SCHRIEVER.

THE method used in this investigation consists of following the evolution of water from powdered set cement when heated under a constant pressure of 7 mm. of mercury. A chemically individual hydrate has a definite vapour pressure at any given temperature, *i.e.*, it will exert a stated pressure at some particular temperature. Let dried set cement be placed in a vessel which is evacuated, and let the temperature be raised until the pressure is 7 mm. If a hydrate is present the pressure in the apparatus will remain constant at the constant temperature until all the hydrate is decomposed; the water vapour evolved is removed by continuous evacuation. If no hydrate is present the

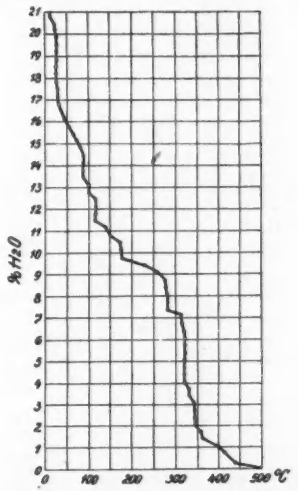


Fig. 1.—Dehydration Isobar of Sample taken 4 m. in front of the Coal-firing Nozzle.

pressure will fall as evacuation proceeds, and the temperature must be further increased to maintain 7 mm. The percentage of water in the cement can be determined by weighing the vessel from time to time in conjunction with a final ignition; it is plotted as ordinate against the temperature of experiment, giving an isobar such as that of Fig. 1, in which the vertical portions ("steps") indicate the existence of a hydrate; that at about 320 deg. C., for example, corresponds to $Ca(OH)_2$.

This method was applied to samples of clinker taken from points 8, 6·5, 5·5, and 4 metres in front of the coal-firing nozzle of a 38.5 m. kiln. Before describing the results, it should be pointed out that at 7 mm. pressure hydrated silica gives "steps" at 30 and 87 deg. C., gypsum at 59 or 73 deg., $Al(OH)_3$ at 200, $Mg(OH)_2$ at 310, and $Ca(OH)_2$ at 390 deg. These temperatures vary in the presence of other compounds.

The 8 m. sample of underburnt cement gave slight steps at 80 and 220 deg., presumably due to silica and $Al(OH)_3$. The 6.5 m. sample gave a pronounced step at 370 deg., $Ca(OH)_2$, and slight steps at 50, 75, and 110 deg. The 5.5 m. sample gave no $Ca(OH)_2$ step, but a series of small steps between 20 and 150 deg., in part due to silica. The 4 m. sample (Fig. 1) gives a pronounced $Ca(OH)_2$ step (320 deg.), with a large number of smaller ones between 20 and 300 deg.; that at 100 deg. is due to silica; those at 175 and 275 deg. cannot at present be attributed to known compounds.

The free lime in the samples of cement material taken at half-metre intervals along the kiln was next determined by the method of Emley, and the results are plotted in Fig. 2. It was found that dissociation of $CaCO_3$ began about 18 m. from the kiln mouth. About 8 m. from the kiln mouth about half the $CaCO_3$ was dissociated, and at this point considerable quantities of free CaO began to be formed, rising to a maximum at 6.5 m., falling again, and rising to a higher maximum at 4 m. (14 per cent. free CaO), finally falling to 2-3 per cent.

Table I gives a summary of the results.

TABLE I.

Distance from Kiln Mouth.	Free Lime Content per Cent.	Dehydration Isobar.	Heat of Reaction on Setting.	Tensile Strength, lb. per sq. in.				Crushing Strength, lb. per sq. in.			
				3 Days.	7 Days.	28 Days.	28 Days Combined Storage.	3 Days.	7 Days.	28 Days.	28 Days Combined Storage.
8m.	Slight	Zeolithic (continuous) curve. No $Ca(OH)_2$ step. Slight steps at 80 and 220 deg. C.	—	—	—	—	—	—	—	—	—
7m.	5	—	Initial slight heat evolution, then gradual heating	0	0	128	185	0	0	200	682
6.5m.	10	Marked $Ca(OH)_2$ step. Indefinite steps between 50 and 120 deg. C.	Initial strong heating (32 deg. C.), then gradual fall	Cement too quick-setting to make test-pieces.							
5.5m.	7	No $Ca(OH)_2$. Indefinite steps between 20 and 150 deg.	Initial moderate heating. A weaker heating after 4 hours ..	128	156	284	441	1,024	1,450	2,233	3,128
4.5m.	12	—	Initial strong heating, then gradual fall....	Cement too quick-setting to make test-pieces.							
4m.	14	Marked $Ca(OH)_2$ step. Slighter steps at 30 and 80 deg. (SiO_2). Slight steps of unknown origin between 100 and 150 and at 280 deg. C.	As above. Heating not quite so pronounced ..	—	—	—	—	—	—	—	—
3.5m.	8	—	Slight initial heating, becoming stronger after 7 hours	242	242	341	583	3,527	4,038	5,432	6,300
0.5m.	3	—	Moderate initial heating, gradually increasing up to 9 hours..	313	327	398	668	3,754	4,721	6,157	7,244

Temperature-time curves of the setting samples, with 3 per cent. added gypsum, were then taken by means of a Gary thermograph. The results will be discussed later. Finally, the crushing and tensile strengths of the gypsumised samples were determined; the crushing strengths of 1 : 3 mortars at 3, 7, and 28 days (air storage and combined storage) are shown in Fig. 3. At 4.5 and 6.5 m. the samples were so quick setting that test-pieces could not be prepared; these points correspond to the free CaO maxima of Fig. 2.

The first point to be noted is that the free CaO maxima at 6.5 and 4.5 m. correspond to pronounced $Ca(OH)_2$ steps in the dehydration isobars and to a very quick-setting cement; the thermograph curves are similar. The fall in free CaO content between the maxima at 4.5 and 6.5 m., which has been confirmed by repetition experiments, is a fact not hitherto known. At 5.5 m. the dehydration isobar shows no $Ca(OH)_2$ step; this step should be present, however, and its absence may be due to experimental error.

The results show (see Fig. 2) that the free CaO formed from the $CaCO_3$ begins to react with the clay at a much lower temperature than that of the

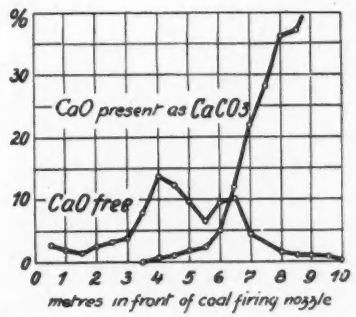


Fig. 2.—Free Lime Content along Kiln.

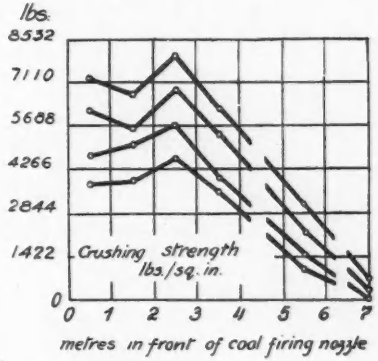


Fig. 3.

clinkering zone. Practically half the $CaCO_3$ is decomposed before free CaO makes its appearance. It may be concluded that the reactions between CaO and clay in the calcining zone proceed in the solid state.

The experiments also throw light on the question whether the hardening of cement is a crystalloid or colloidal process. The dehydration isobars show that definite chemical hydrates exist in newly set cement, and that their formation continues with time. On the other hand, the continuous portions of the curves point to colloidal phenomena. It is therefore concluded that hardening depends partly on gel formation and partly on crystal formation.

[These notes are translated from an article in *Zement*, p. 31, 1932.]

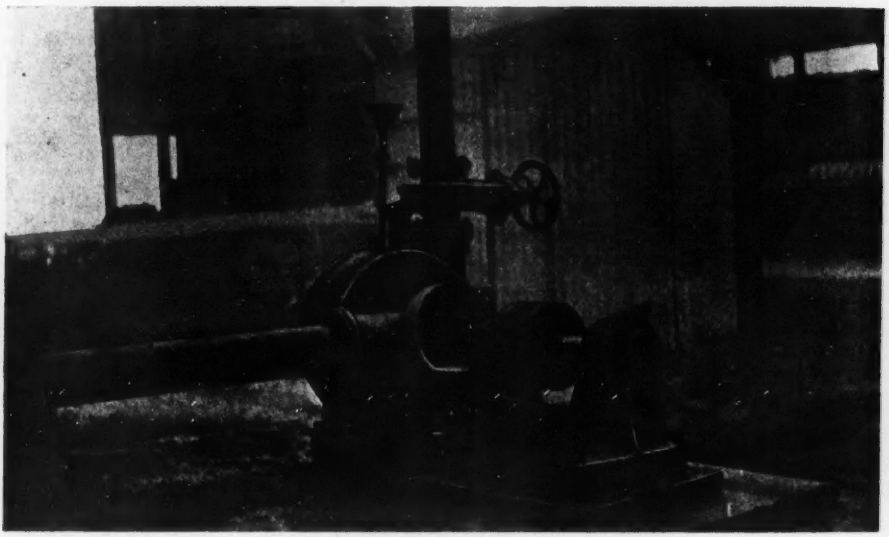
Cement Production in Brazil.

The production of Cia Brasileira de Cemento Portland for 1931 amounted to 163,800 tons. The company's third and largest kiln was put into operation during the year. The annual capacity of the works at Perus, Sao Paulo, is now 200,000 tons.

A New Centrifugal Pump for Cement Slurry.

IN an attempt to produce a centrifugal pump that will stand up permanently to the heaviest duty under the most drastic conditions, with undiminished efficiency of a perfectly balanced, smooth-running and silently operating machine, Messrs. Edgar Allen and Co., Ltd., of Sheffield, have produced a development of their well-known "Stag" pump.

In this machine the impeller shroud on the suction side (on both sides in special circumstances) forms a sealing drum overlapping the peripheral edge of a stationary sealing disc, which has a central trunnion extended to form a renewable liner to the pump suction compartment and provided with a ring path enveloping and adjustably adjacent to the suction eye-ring or trunnion of the impeller. The rim of the sealing drum effectually opposes inward circulation



Suction Side of Pump.

of liquid under pressure, and prevents leakage in close circuit about the suction eye. Thus the pump provides permanent efficiency with minimum wear and tear.

The suction compartment is on the shaft side of the impeller (except in special circumstances when the suction compartment occupies both sides) and has, therefore, no stuffing-box under working pressure. The impeller shaft passes through a stuffing-box packed only against atmospheric pressure to prevent entrainment of air with suction.

Provision is made for admission of clean water at low pressure through a hard-metal neck bush between the suction compartment and the gland packings. Further, a centrifugal seal is provided in the suction compartment, comprising an "excluder" in the form of a small-vaned impeller rotating in a recessed chamber of the liner, with its vanes facing the neck bush to receive inflowing clean water therefrom, and by centrifugal action to create a hydraulic pressure

at its periphery capable of resisting entry of pulp even though that may be fed to the pump under a considerable head, as when the pump is set below the level of pulp in the supply tank.

The pump shaft is fitted with a renewable sleeve of special steel which is ground true and rendered "glass-hard" on the wearing surface by a treatment by which wear in the glands is practically avoided, and true running and air-tightness are maintained for long periods.

Only in special circumstances is it necessary to break pipe joints or to remove gauges or cocks to gain access to the interior working parts of the pump. The pump cover is secured by eight studs to the permanent pump case and by set screws to the renewable pump-case liner, reinforced by three locating set screws. By "slacking-back" the locating screws and removing the nuts

Centrifugal Pump with Cover Removed.

from the studs, the pump cover, with case liner attached, is removable, thereby disclosing the impeller, which can easily be disconnected from its shaft. If a spare impeller is available the pump can be ready for running again within half an hour after stopping, although in the case of a large pump the removable parts of which are too heavy to be handled without mechanical aid. The gland is made in halves, assembled with two small set screws, and tightened with nuts on two studs; the removal of these gives access to the packings, the lantern ring, and the neck bush, which operation is facilitated by releasing the ring-oiling pedestal from its seat on the pump bedplate and sliding it along the pump shaft away from the stuffing box to give more room for withdrawing the old packings and inserting new ones.

Endwise adjustment of impeller location is obtained by removing the thrust bearing cap, slackening the adjusting and locking nuts, and (after making the

small adjustment required) tightening them again with the special keys provided. When it is required to renew the shaft sleeve, removal of the thrust bearing cap, ball and roller bearings, adjusting and lock nuts, permits the shaft to be withdrawn through the pump case for a sufficient distance for the removal and replacement of the sleeve; or the shaft may be drawn in the opposite direction until clear of the stuffing box and gland.

The standard pump is built "right hand," i.e., when standing at the thrust bearing end of the pump shaft and looking towards the impeller end of the shaft the direction of rotation is counter clockwise and the delivery branch is normally at the observer's right hand. "Left hand" pumps are supplied to order. The pump case may take any one of eight positions at 45 deg. intervals, so that the delivery branch may point upwards or downwards, undershot, overshot, or midway between, in any direction. The pump suction compartment is similarly capable of taking up any of eight positions, and the suction branch may receive its feed horizontally, vertically, or midway between, from any direction.

When required for heavy duty and large capacity the pump is built with twin suction so that the impeller, working between two compartments under the influence of vacuum (though only one compartment or both may be used for feeding the pump), is running in axial balance and free from end-thrust.

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Cement Imports in Finland.

It is stated in the "Survey of Foreign Trade in Finland," published by the Department of Overseas Trade, that cement imports have declined from 24,000 tons in 1930 to 4,000 tons in 1931. This is accounted for by the depression in the building trade and the increased competition from Finnish cement.

Grecian Cement Imports.

The imports of cement into Greece from Yugoslavia in 1931 and 1930 were 16,931 tons and 29,144 tons respectively. Imports from Russia amounted to 11,769 tons and 26,482 tons in these two years, and from other countries the amounts in 1931 and 1930 were 13,848 tons and 9,028 tons respectively. The total imports were 42,548 tons in 1931 and 64,654 tons in 1930.

Cement Imports in Palestine.

It is stated in the annual report issued by the Department of Customs, Excise and Trade, Haifa, Palestine, that cement imported into Palestine in 1931 amounted to 4,725 tons, compared with 5,154 tons in 1930, and that this was chiefly white cement. Exports from Palestine were 8,941 tons in 1931 and 12,357 tons in 1930.

Recent Patent Applications.

Manufacture of Cementitious Material. BERRY, H. No. 350,129.

Rotary Kilns for Burning Cement. VICKERS-ARMSTRONGS, LTD., and PARKER, L. D. No. 351,283.

No. 361,901.—**W. W. Triggs** (EDDYSTONE CEMENT CORPORATION).—Manufacture of cement.

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Trade Notices.

Chain Driving Diagrams.—We have received from The Renold & Coventry Chain Co., Ltd., a new booklet entitled "Chain Driving Diagrams." This booklet has been compiled to satisfy a long-felt want amongst engineers and designers, as hitherto no adequate information concerning chain driving practice has been included in the recognised engineers' text books. The booklet is made up diagramatically, which not only eliminates misunderstanding of the terms used but also enables the availability of chain gear to be readily visualised in relation to any particular transmission problem. We understand copies of this particularly useful booklet will be sent free on request to readers of this journal. The address is The Renold & Coventry Chain Co., Ltd., Renold Works, Didsbury, Manchester.

Visco Filters.—A new catalogue dealing with air filtration plants has been issued by the Visco Engineering Co., Ltd., of 162, Grosvenor Road, London, S.W.1. The brochure contains much of interest to all users of air filters, and besides describing the well-known "Visco" plant it gives a great deal of general information. Copies will be sent free on request.

Change of Telephone Numbers.—The telephone number of the Associated Portland Cement Manufacturers, Ltd., the British Portland Cement Manufacturers, Ltd., and the Cement Marketing Co., Ltd., at Portland House, Tothill Street, S.W.1, has been changed from Victoria 9980 to Whitehall 2323. The Exchange of Messrs. Concrete Publications, Ltd., has been altered from Victoria to Whitehall, but the number is still 4581.

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